

## Carbon nanotube thermal interfaces enhanced with sprayed on nanoscale polymer coatings

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# Carbon nanotube thermal interfaces enhanced with sprayed on nanoscale polymer coatings

John H Taphouse<sup>1</sup>, Thomas L Bougher<sup>1</sup>, Virendra Singh<sup>1</sup>,  
Parisa Pour Shahid Saeed Abadi<sup>1</sup>, Samuel Graham<sup>1,2</sup> and  
Baratunde A Cola<sup>1,2</sup>

<sup>1</sup> George W Woodruff School of Mechanical Engineering, Georgia Institute of Technology, 771 Ferst Drive, Atlanta, GA 30332, USA

<sup>2</sup> School of Materials Science and Engineering, Georgia Institute of Technology, 771 Ferst Drive, Atlanta, GA 30332, USA

E-mail: [cola@gatech.edu](mailto:cola@gatech.edu)

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## Abstract

Vertical carbon nanotube (CNT) forests bonded at room temperature with sprayed on nanoscale polymer coatings are found by measurement to produce thermal resistances that are on a par with those of conventional metallic solders. These results are achieved by reducing the high contact resistance at CNT tips, which has hindered the development of high performance thermal interface materials based on CNTs. A spray coating process is developed for depositing nanoscale coatings of polystyrene and poly-3-hexylthiophene onto CNT forests, as a bonding agent that mitigates thermal resistance by enhancing the area available for heat transfer at CNT contacts. Resistances as low as  $4.9 \pm 0.3 \text{ mm}^2 \text{ K W}^{-1}$  are achieved for the entire polymer coated CNT interface structure. The suitability of the spray coating process for large-scale implementation and the role of polymer and CNT forest thickness in determining the thermal resistance are also examined.

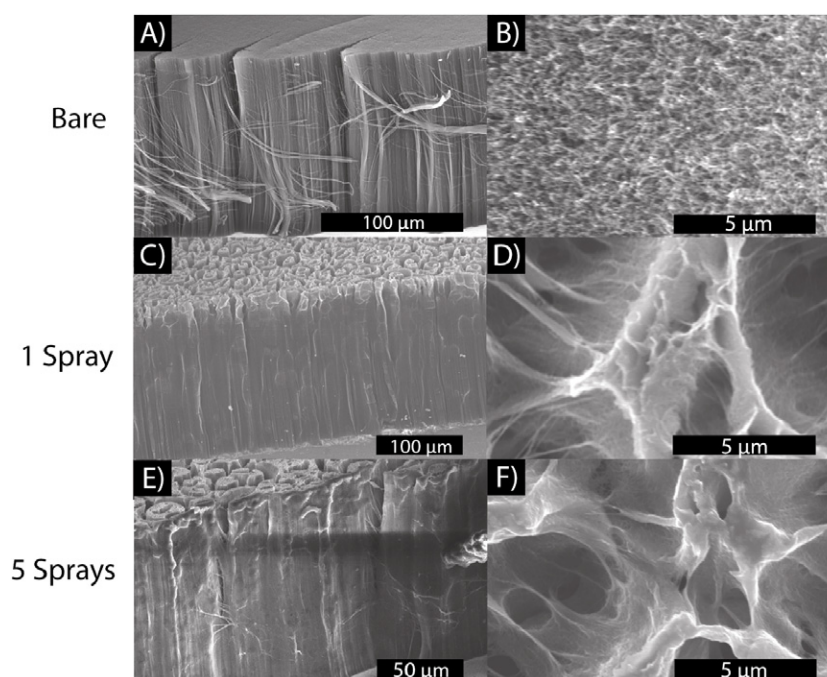
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(Some figures may appear in colour only in the online journal)

## 1. Introduction

As the semiconductor industry continually strives to increase the power density of single-chip packages, thermal management remains a critical challenge toward realizing both performance and reliability metrics. One of the primary bottlenecks inhibiting effective thermal management arises from the several interfaces that can exist between the chip and heat sink. Specifically, the thermal resistance of the thermal interface materials (TIMs) that are currently used to bridge these interfaces must be decreased [1]. Carbon nanotubes (CNTs), with their extraordinarily high axial thermal conductivity, have generated tremendous interest as candidates for providing low resistance TIMs [2–13]. The most promising CNT TIMs produced to date have

consisted of vertical forests, where the CNT axis is nominally aligned orthogonal to the contact surfaces, providing maximum conductivity in this direction. This alignment also provides maximum mechanical compliance along the contact surfaces, mitigating deleterious effects of mismatches in the coefficients of thermal expansion of the interface materials. However, even in this arrangement CNT TIMs demonstrated limited performance due to the presence of high thermal contact resistances between the CNT tips and opposing surfaces [13, 14]. Efforts to mitigate such contact resistances have centered around different methods for bonding the CNT tips to the opposing surface and have included metallic film bonding [6, 7, 13, 15], palladium nanoparticle bonding [8], and wet chemical modification of Si [11]. While these techniques have in some cases produced CNT TIMs with



**Figure 1.** SEM images of bare and polymer spray coated CNT forests. The amount of polymer visible on the CNT arrays increases with the number of sprays. No morphological differences were observable between PS and P3HT. (C) and (E) were spray coated with P3HT, and (D) and (F) were spray coated with PS.

thermal resistances approaching those of conventional TIMs, they often require high cost materials, such as Au or In, and processing, including metal thin film deposition, high temperature and high pressure bonding, and even exposure to microwave radiation, that are not favorable for large-scale implementation. In this work we explore a potentially scalable and low cost process that utilizes spray coating to deposit thin polymer films onto the tips of CNTs for bonding at room temperature.

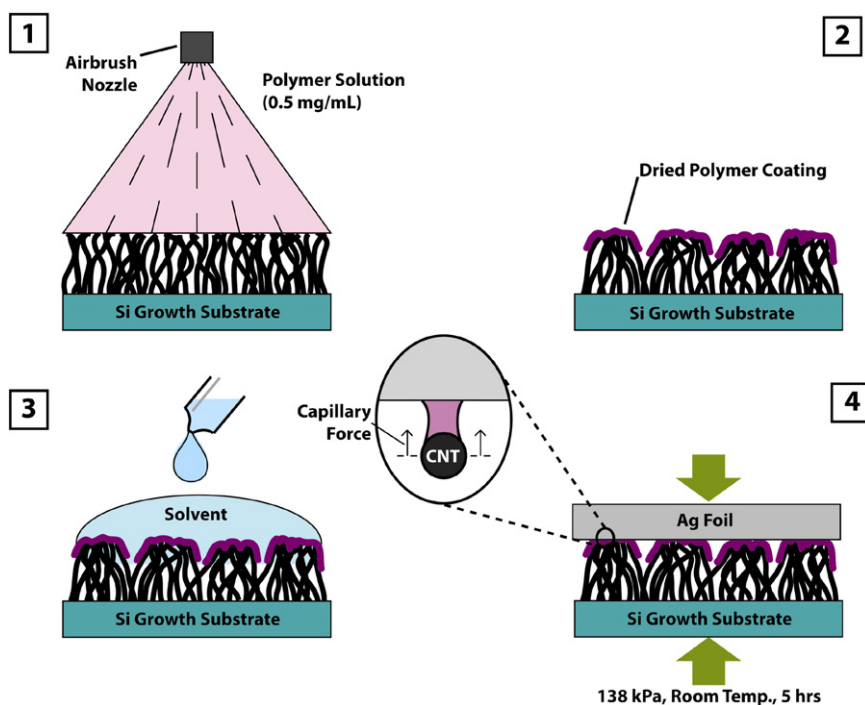
Polymers were dissolved into solution and spray coated onto the tops of vertical CNT forests grown on Si substrates to evaluate the novel CNT TIM enhancement approach. The spray coated CNTs were then bonded to Ag foil substrates by wetting the interface with solvent, and allowing it to dry under moderate pressure at room temperature. The total thermal resistance of the interface—including the contact resistance of the polymer bonded interface, the resistance of the CNT forest, and the contact resistance at the growth substrate interface—was measured using a photoacoustic method [14, 16, 17]. Two polymer systems were studied: the first, polystyrene (PS) was chosen since it is a low cost widely used aromatic polymer that is chemically stable at device operating temperatures [18]; the second, poly-3-hexylthiophene (P3HT) was chosen because it has been shown to interact strongly with CNTs through  $\pi$ - $\pi$  bonding and by preferentially wrapping around the nanotube axis [19–21]. Additionally, due to its conjugated back bone, P3HT is chemically stable at higher temperatures as compared to PS [22]. The height of the CNT forest and the quantity of polymer sprayed were varied individually in an effort to understand their influence on the thermal resistance of the interface. To demonstrate how the spray coating process might be scaled for manufactured

production, CNT forests were grown on both sides of Al foil to create a thermal interposer, similar to that created by Cola *et al* [4]. The CNT coated foil interposer eliminates the necessity to grow or transfer print CNTs directly onto the back of the chip or packaging. The CNT growth and spray coating process can instead take place separately on the metal foil, before being incorporated into the electronic package.

## 2. Experimental section

### 2.1. CNT synthesis, spray coating, and bonding

Vertical forests of CNTs were grown on single-crystal Si substrates diced into  $1 \times 1 \text{ cm}^2$  pieces. Ti, Al, Fe films in thicknesses of 30, 10, 3 nm were evaporated onto the Si as support and catalyst layers for CNT growth. Afterwards the CNTs were grown using a low pressure chemical vapor deposition process at  $850^\circ\text{C}$  and 10 mbar in an Aixtron Black Magic© reactor with  $\text{C}_2\text{H}_2$  as the carbon source gas. The growth time was varied from 3 to 15 min to grow forests of multiwall CNTs ranging from 5 to  $150 \mu\text{m}$  in height with an average CNT diameter of 8 nm. Scanning electron micrograph (SEM) images of representative CNT forests are shown in figures 1(A) and (B). CNT forests were also grown on both sides of  $10 \mu\text{m}$  thick Al foil (Alfa Aesar 41798) to create a thermal interposer. An identical growth process was employed except that 100 nm of Ni was added to the bottom of the catalyst stack as a diffusion barrier and the temperature of the growth stage was lowered to  $750^\circ\text{C}$  (a pyrometer measured the actual sample temperature to be approximately  $630^\circ\text{C}$ , which is less than the melting temperature of Al).



**Figure 2.** Illustration of the polymer spray coating and bonding process. (1) Spray deposition of polymer onto the top of the CNT forest. (2) The polymer coating dries, causing clumping of the CNT tips. (3) Solvent ( $\text{CHCl}_3$ ) is applied to the top of the CNT forest to wet and reflow the polymer coating. (4) Still wet polymer coating is brought into contact with Ag foil and placed under 138 kPa of pressure for 5 h while the interface dries, during which time capillary forces likely draw additional CNTs towards the interface.

For spray coating polymer solutions,  $0.5 \text{ mg ml}^{-1}$  of P3HT (regioregular, Sigma Aldrich 445703) or PS (MW 35 000, Sigma Aldrich 331651) were prepared by sonicating or stirring for 5 min into  $\text{CHCl}_3$ . The solutions were sprayed in 1 ml increments onto the CNT tips using an airbrush (Iwata Eclipse HP-CS Gravity Feed) with 280 kPa  $\text{N}_2$  as the carrier gas. The airbrush was positioned 10 cm above the CNT forest so that the conical spray profile of the airbrush deposited polymer over an area slightly larger than the area of the CNT forest sample. It is difficult to quantify the fraction of polymer deposited onto the CNT forest for each 1 ml spray; therefore we refer to the quantity of polymer applied to each CNT forest in terms of the number of 1 ml sprays. The number of sprays was altered among 1, 2, and 5 in order to examine the effects of the quantity of polymer on the resultant thermal resistance of the bonded CNTs. As is shown in figure 1, the spray coating process restricts the deposition of polymer to the CNT tips and limits clumping due to capillary forces associated with the drying of the solvent (figure S1 available at [stacks.iop.org/Nano/24/105401/mmedia](http://stacks.iop.org/Nano/24/105401/mmedia)).

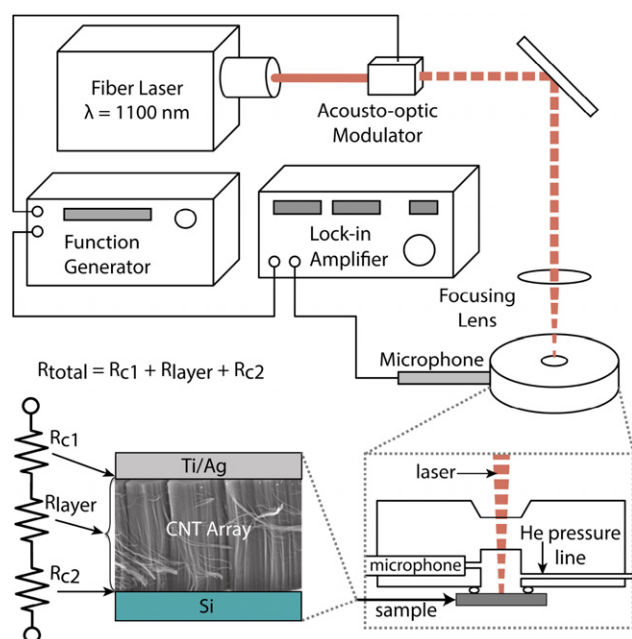
Spray coated CNTs on Si substrates were bonded to  $1 \times 1 \text{ cm}^2$  pieces of 25  $\mu\text{m}$  thick Ag foil (Alfa Aesar 11498). The Ag foil acts as a thermally conductive top substrate for photoacoustic measurements. Before bonding, 80 nm of Ti was evaporated onto the top of the Ag foil for absorbing the laser energy ( $\lambda = 1100 \text{ nm}$ ). To bond the polymer coated CNT forests to the Ag foil, the CNT forests were first wetted with a few droplets of  $\text{CHCl}_3$  to reflow the polymer, and then promptly placed into contact with the Ag foil under 138 kPa of pressure. The interface was allowed to dry for at least

5 h under ambient conditions before the load was removed. The entire spray coating and bonding process is shown schematically in figure 2. Transmission electron micrographs (TEMs) taken of CNTs after bonding captured P3HT chains wrapped around individual CNTs (figure S2 available at [stacks.iop.org/Nano/24/105401/mmedia](http://stacks.iop.org/Nano/24/105401/mmedia)). This agrees with prior observations of strong affinity between CNTs and P3HT [19–21]. In a process similar to that described above, both sides of the CNT coated foil interposer structures were bonded between quartz substrates and Ag foil. However, the bonding pressure was increased to 580 kPa for observing the maximum potential of the structure.

## 2.2. Photoacoustic characterization

The thermal resistance of the polymer bonded structures was measured using a photoacoustic (PA) method [14, 16, 17], shown in figure 3. The PA method uses a modulated laser beam to periodically heat the sample structure. As the heat is absorbed at the sample surface it is conducted both downward through the sample and upward into an acoustic chamber filled with He gas. The periodic nature of the heating causes periodic pressure fluctuations in the He gas layer that are detected using a microphone embedded in the chamber wall. The phase delay of the pressure signal relative to the heating pulse is used to fit unknown thermal properties in a theoretical model for 1D heat conduction through layered media. For this work it was used to extract the total thermal resistance of the CNT interface. In addition to bonded interfaces, two other sample configurations were studied in an effort to





**Figure 3.** Schematic of the photoacoustic system and sample configuration. The thermal resistance reported is the total resistance of the CNT interface.

better understand the effects of the polymer on the interface resistance: dry contact: as grown bare CNT forests in dry contact with the Ag foil; and polymer coated dry contact: CNT forests spray coated with varying quantities of polymer that were allowed to dry before being placed into dry contact with the Ag foil.

### 3. Results and discussion

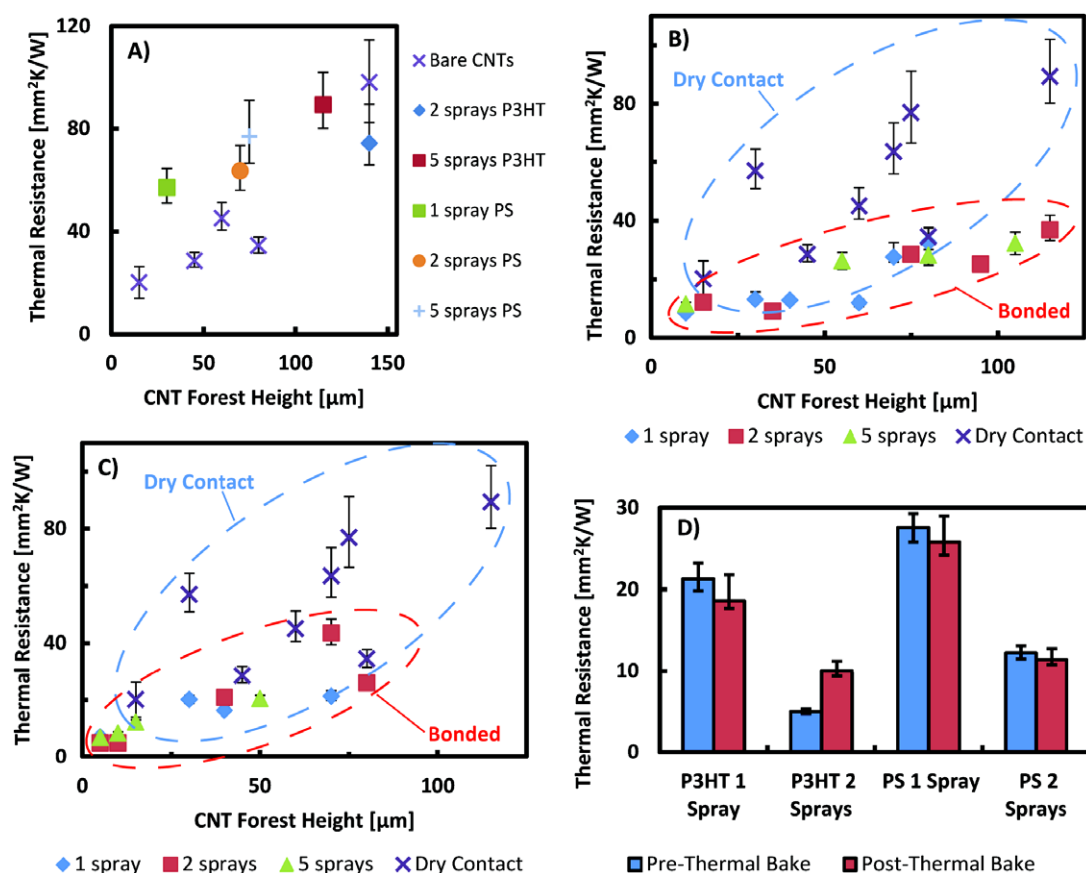
The total thermal resistance for all three sample configurations (dry contact, polymer coated dry contact, and polymer bonded) is shown in figures 4(A)–(C). Each of these total resistances is the sum of the contact resistance at the CNT tips, the intrinsic thermal resistance of the CNT forest, and the contact resistance at the CNT growth substrate. It is important to note that the base pressure of the He gas in the PA cell can be adjusted to alter the pressure applied to the interface during the measurement. Measurements for all three sample configurations were conducted at cell pressures of both 7 and 138 kPa. All results for the dry contact sample configurations shown in figures 4(A)–(C) are those collected at a cell pressure of 138 kPa. Data collected on dry contact and polymer coated dry contact samples at 7 kPa were inconsistent, likely due to inconsistent and/or poor contact conditions at the interface under this light load. The data collected on bonded samples did not exhibit significant changes with the pressure in the PA cell, indicative of a well-bonded interface, and are shown at 7 kPa in figures 4(B) and (C). All of the data from figure 4(A) for samples less than 125  $\mu\text{m}$  in height are shown in figures 4(B) and (C) for comparison. These data are labeled as ‘Dry Contact’, although the set includes both the dry contact and the polymer coated dry contact data.

The thermal resistance increases with CNT height for all sample configurations. The thermal resistance of polymer

coated dry contact samples was higher than those of all but one of the bare CNT dry contact samples. Because the nanoscale polymer coating has relatively negligible thermal resistance, the difference in performance likely stems from the fact that adding the dried coating of polymer to the interface stiffens the top of the forest, effectively reducing the extent to which it conforms to the Ag foil. This reduces the contact area and increases the thermal contact resistance. Bonding with both P3HT and PS reduced the thermal resistance of the interface, with the largest reductions occurring at the tallest forest heights. For example, a 58% reduction was observed for PS bonding of forests 115  $\mu\text{m}$  in height. The polymer bonded samples exhibited a weak trend of increased thermal resistance with the number of sprays. However, the trend is considered to be of low significance because it is violated for several samples, and because the magnitude of the differences in resistance with number of sprays is of similar order to the distribution of the data. The lowest measured resistances for P3HT bonded, PS bonded, and bare CNT dry contact samples were  $4.9 \pm 0.3 \text{ mm}^2 \text{ K W}^{-1}$  (10  $\mu\text{m}$  tall forest with two sprays),  $8.5 \pm 0.5 \text{ mm}^2 \text{ K W}^{-1}$  (10  $\mu\text{m}$  tall forest with one spray),  $20 \pm 6 \text{ mm}^2 \text{ K W}^{-1}$  (15  $\mu\text{m}$  tall forest), respectively.

The reported PA measurement uncertainties have contributions from both the resolution of the experimental setup, estimated to be  $\pm 1^\circ$  in the measured phase shift, and the repeatability, i.e. variations in the thermal resistance at different measurement locations on a sample. The error bars include contributions from both sources for the dry contact and polymer coated dry contact data. The error bars represent only the resolution of the measurement technique for bonded samples and are too small to be seen for the majority of the data points. The uncertainty associated with repeatability is captured by the distribution of the data for bonded samples.

Thermal degradation, due to chemical stability of the polymers at elevated temperatures, is also a significant concern for polymer based TIMs [23]. Hence, four of the samples, two P3HT bonded and two PS bonded, were subsequently thermally baked at 130  $^\circ\text{C}$  and 680 mbar for 110 h in a vacuum oven to mimic high temperature operating conditions. There was no statistically significant change in the thermal resistance of the samples between before and after baking (figure 4(D)) for three of the four sample types tested. There was a slight increase in the thermal resistance of the two-spray P3HT sample after thermal baking. Both PS and P3HT have been demonstrated to be chemically stable at temperatures above 130  $^\circ\text{C}$  [18, 24], so the increase in resistance observed for the two-spray P3HT samples is likely due to other factors such as local spot-to-spot variation in the CNT forest morphology or local loosening of the interface bond during sample handling. The overall results from thermal baking suggest that the polymer coatings used here are stable over the temperature range studied and that the process may be suitable for integration with high power density devices. The thermal resistances of bare CNT coated foil interposers in a dry contact arrangement were measured to be  $21 \pm 4 \text{ mm}^2 \text{ K W}^{-1}$ . The thermal resistances of interposers spray coated and bonded with one spray of P3HT were measured to be  $9 \pm 2 \text{ mm}^2 \text{ K W}^{-1}$ ; this is an



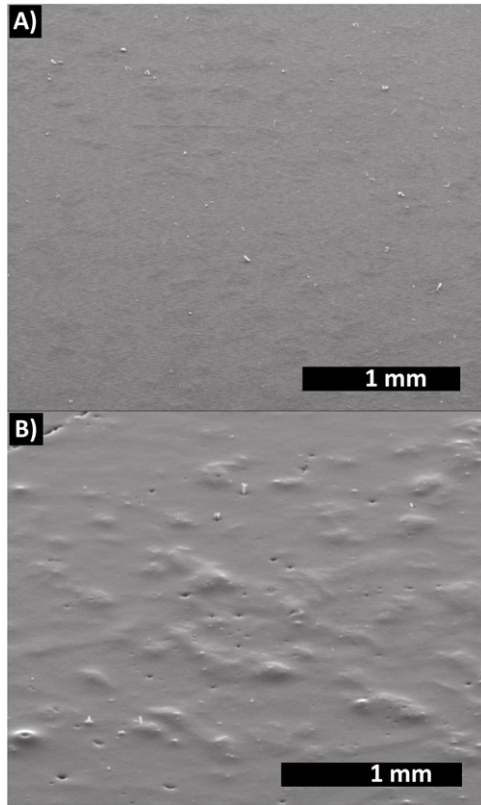
**Figure 4.** (A) Thermal resistance of polymer coated and bare CNT arrays in dry contact. (B) Thermal resistance of PS bonded interfaces (PA cell pressure = 7 kPa) compared to the dry contact interfaces (PA cell pressure = 138 kPa). (C) Thermal resistance of P3HT bonded interfaces (PA cell pressure = 7 kPa) compared to dry contact interfaces (PA cell pressure = 138 kPa). (D) Thermal resistance of polymer bonded samples before and after being baked at 130 °C for 110 h.

approximate twofold decrease in resistance. Three samples of each configuration were produced and the uncertainty in the thermal resistance was dominated by the variability between samples.

The thermal resistance increased with increasing CNT forest height for each of the sample configurations studied. One cause for the observed trend is apparent: increasing the height of the CNT forest increases the amount of material through which the heat must travel, hence increasing the resistance of the CNT layer itself. A second cause is more subtle and is specific to the CNT growth process. During the CNT growth, certain regions of the forest grow at greater or lesser rates compared to the average growth rate due to slight discrepancies in the condition of the catalyst particles and their access to the carbon gas source. As the forest grows, the difference in height between the different growing regions is increased, resulting in decreased height uniformity with growth time. The decreased uniformity of the CNT forest is equivalent to an increase in the surface roughness of the CNT forest. This increase in surface roughness can be observed in figure 5, and leads to a decrease in the contact area at the interface and an increase in the thermal contact resistance. Additional factors related to growth process, such as CNT pullout at the growth substrate and changes in morphology

with growth time, may also contribute to increases in the thermal resistance with increasing forest height [25].

Since the polymer spray coating process was only observed to apply polymer to the CNT tips, it is reasonable to assume that the bonding process only leads to significant changes in the thermal contact resistance at the CNT tips, and that the thermal resistance of the CNT forest and the thermal contact resistance at the growth substrate are not affected significantly. Overall, bonding with both P3HT and PS was observed to decrease the resistance of CNT forests comparably, ruling out any contributions from polymer structure or differences in the nature of the polymer–CNT interactions. Therefore, to better understand the source of the reduction in the thermal resistance, we consider how the polymer might affect the heat transfer between a single CNT in side contact with the Ag foil [26], as shown in figure 6. To observe the structure of bonded interfaces, spray coated CNT forests were bonded to Si substrates, to which the adhesion was negligible, then disassembled and examined using SEM (figures 6(A) and (B)). On the basis of the SEM images, the configuration of a polymer bonded CNT, shown in figure 6(D), was assumed for the subsequent theoretical heat transfer analysis. Heat transfer for the case without any polymer has been analyzed by several investigators and shown to be dominated by the ballistic surface resistance [26,



**Figure 5.** SEM images comparing the surface roughness of short and tall CNT forests. (A) Top view of a 5  $\mu\text{m}$  tall forest, and (B) top view of a 70  $\mu\text{m}$  tall forest.

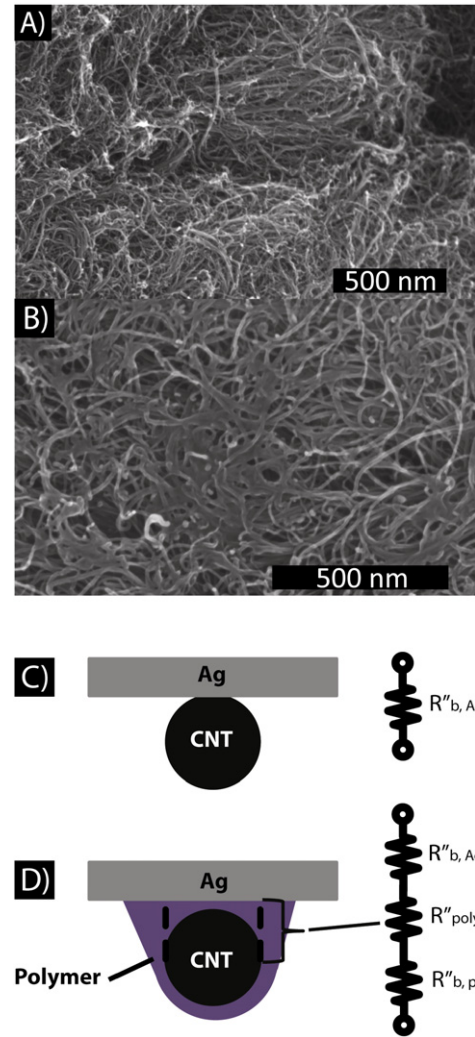
27]. The ballistic resistance considers the flow of phonons through the contact as free molecular flow through an orifice with a transmission coefficient derived from diffuse mismatch assumptions and Chen's gray medium approach [28]. The contact area normalized ballistic resistance,  $R''_b$ , is given by

$$R''_b = \frac{4(C_{l,1}v_{g,1} + C_{l,2}v_{g,2})}{C_{l,1}v_{g,1} \times C_{l,2}v_{g,2}} \quad (1)$$

where  $C_l$  is the lattice specific heat,  $v_g$  is the phonon group velocity, and the subscripts 1 and 2 are used to denote materials on opposite sides of the interface. Taking  $v_{g,\text{CNT}} = 1000 \text{ m s}^{-1}$  as the through basal plane velocity for graphite [29],  $C_{l,\text{CNT}} = 1582 \text{ kJ m}^{-3} \text{ K}^{-1}$ ,  $v_{g,\text{Ag}} = 1640 \text{ m s}^{-1}$ , and  $C_{l,\text{Ag}} = 2362 \text{ kJ m}^{-3} \text{ K}^{-1}$ , the contact area normalized resistance for a single Ag–CNT contact is [30, 31]  $R''_{\text{Ag-CNT}} = 3.6 \times 10^{-3} (\text{mm}^2 \text{ K W}^{-1})$ . When polymer is added as is shown in figure 6(D), the resistance of the interface can be approximated by the sum of the ballistic resistance between the Ag and the polymer, the ballistic resistance between the polymer and the CNT, and the resistance of the polymer layer itself. The contact area normalized resistance of the polymer layer is given by the classical expression

$$R''_{\text{poly}} = \frac{l}{k_{\text{poly}}} \quad (2)$$

where  $l$  is the thickness of the polymer layer and  $k_{\text{poly}}$  is the polymer thermal conductivity. Assuming  $l = 10 \text{ nm}$ ,



**Figure 6.** (A) SEM image of the top of a CNT forest after one spray of P3HT and bonding. (B) SEM image of the top of a CNT forest after five sprays of P3HT and bonding. ((C), (D)) Illustrations of CNT dry contact and polymer bonded contact configurations respectively and the associated thermal resistance network.

which is reasonable on the basis of the polymer accumulation observed at CNT tips in figures 6(A) and (B), and taking PS as the polymer since its properties are widely known,  $k_{\text{PS}} = 0.25 \text{ W m}^{-1} \text{ K}^{-1}$ , the contact area normalized resistance for a polymer coated CNT becomes  $R''_{\text{Ag-PS-CNT}} = 4.6 \times 10^{-2} (\text{mm}^2 \text{ K W}^{-1})$ . This result indicates that under the prescribed assumptions the polymer actually increases the contact area normalized thermal resistance by an order of magnitude. The resistance of the polymer layer,  $R''_{\text{poly}}$ , causes most of this increase because of its low thermal conductivity. Therefore, adding the polymer must increase the contact area by greater than an order of magnitude as compared to CNT dry contact to reduce the total resistance of the interface. Assuming a van der Waals interaction and elastic contact, a CNT with a diameter of 8 nm will only have a width of contact of approximately 1 nm with the Ag foil [29, 32]. Should the polymer fill the interstitial space between the CNT and the foil to the extent of the CNT diameter, it would increase the contact area by a factor of 8.



Measurements of the shear attachment strength of CNT forests that were polymer bonded to glass slides coated with Ag revealed an average attachment strength of 290 kPa (see the supplemental file for details available at [stacks.iop.org/Nano/24/105401/mmedia](http://stacks.iop.org/Nano/24/105401/mmedia)). This is a more than threefold increase over reported values for shear attachment strength of CNTs in dry contact with glass slides [33]. The increase in attachment strength from polymer bonding corresponds to an increase in area that is similar in magnitude to the increase in area that would be achieved from filling the space between the CNT and Ag with polymer (figure 6). This suggests that adding the polymer might increase the contact area in this manner. Furthermore, Cola *et al* estimated that the real contact area in CNT forest TIMs is only  $\sim 1\%$  of the apparent area [26]. Similarly, Panzer *et al* estimated that only 0.35% of the volume fraction of CNT forests effectively participate in heat transfer in CNT forest TIMs [12]. Therefore, the polymer might also increase the contact area by engaging additional CNTs, especially since capillary forces associated with drying of solvent during the bonding process likely draw additional CNT tips closer to the interface as illustrated in figure 2.

It is pertinent to note that in the above calculations the ballistic resistance assumes that the interface is bonded perfectly. This assumption is clearly not valid for the weak van der Waals interactions present at both the dry contact and polymer bonded interfaces. As a result, the above calculations for the CNT–Ag, CNT–polymer, and Ag–polymer contacts underpredict the thermal resistance significantly. The actual resistances of the contacts might be one to two orders of magnitude higher than the estimates based on perfect bonding, because phonon transmission is attenuated by weak interfacial bonding [26, 34, 35]. As a result, the resistance of the polymer layer,  $R''_{\text{poly}}$ , at a thickness of 10 nm would be on par with or an order of magnitude less than the surface resistances at van der Waals contacts. The higher end of the expected surface resistance considering van der Waals bonding would allow the polymer layer to be as thick as several 100 nm without dominating the total resistance at CNT–polymer–Ag contacts; the polymer layer could be even thicker if its bulk thermal conductivity was enhanced by nanostructuring [36]. While it is difficult to accurately calculate or measure the thermal resistance of a CNT tip in both dry contact and polymer bonded arrangements, the simple analysis presented here has shown that adding polymer does not reduce the area normalized thermal resistance of CNT contacts; it instead extends the area available for heat transfer at the contacts to CNT tips.

#### 4. Conclusion

Polymer spray coating and bonding was demonstrated as an effective means for increasing the contact area and reducing the thermal resistance of CNT forest thermal interfaces. The bonding process added nanoscale coatings of polymer around individual CNT contacts and potentially pulled, through capillary action, additional CNTs close to the interface to increase the contact area. Spray coating with polystyrene and poly-3-hexylthiophene produced CNT TIMs with thermal

resistances of  $8.5 \pm 0.5$  and  $4.9 \pm 0.3 \text{ mm}^2 \text{ K W}^{-1}$  respectively, comparable to conventional solder TIMs. The thermal resistances did not change significantly after baking at  $130^\circ\text{C}$  for 110 h. The thermal resistances of dry and polymer bonded CNT interfaces were found by measurement to increase with CNT forest height because of the increased surface roughness of taller forests. The relatively low cost of polystyrene in addition to favorable bonding conditions, i.e. room temperature and low pressure (138 kPa), make the spray coating and bonding process attractive for large-scale implementation. As a demonstration of how the process might be scaled, CNT forests were grown on both sides of Al foil to create an interposer material with a thermal resistance of  $9 \pm 2 \text{ mm}^2 \text{ K W}^{-1}$  when bonded.

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